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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08G 61/10, C07C 43/23, 39/24, 43/225	A1	(11) International Publication Number: WO 96/28491 (43) International Publication Date: 19 September 1996 (19.09.96)

(21) International Application Number: PCT/US96/02550

(22) International Filing Date: 7 March 1996 (07.03.96)

(30) Priority Data:
08/402,278 10 March 1995 (10.03.95) US

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(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: SOLUBLE FLUORINATED POLY-P-PHENYLENES

(57) Abstract

Disclosed are poly-p-phenylenes which have perfluoroalkoxy and perfluoroalkyl substituents, their copolymers and the precursors to these polymers. Polymers produced herein are useful as membranes, coatings, fibers and articles.

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TITLE

SOLUBLE FLUORINATED POLY-P-PHENYLENES

FIELD OF THE INVENTION

This invention concerns poly-p-phenylenes which have perfluoroalkoxy and perfluoroalkyl substituents, their copolymers and the precursors to these polymers, including the perfluoroalkoxy- and perfluoroalkyl-substituted hydroquinones and triflate derivatives, and the corresponding biphenyl systems. Polymers produced herein are useful as membranes, coatings, fibers and articles.

TECHNICAL BACKGROUND

There is an ever-increasing need in electronic applications for polymeric materials which display enhanced physical properties, especially in the areas of lower dielectric constant, low moisture absorption and low coefficient of thermal expansion (CTE).

Polyphenylenes are highly rod-like materials and are therefore likely to give films with low in-plane CTE. Typical polyphenylenes are highly insoluble, intractable materials and therefore extremely difficult to process into useful products. Thus, it would be useful to develop materials that retain the low CTE but have better processability characteristics.

The polymers and copolymers of the present invention melt without decomposition and show good processibility because of their solubility in selected polar organic solvents (e.g., THF). This allows the casting of films and other shaped articles. In addition, copolymerization with appropriate flexibilizing comonomers could result in improved elongation of these highly rod-like homopolymers while maintaining, to a large extent, the other desirable properties of the backbone. This invention also affords a soluble polymer without the loss of the desired rigidity or an increase in the dielectric constant.

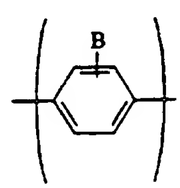
Rehahn, et al., Makromol. Chem. 191, p. 1991-2003 (1990) and Tour, et al., J. Amer. Chem. Soc. 113, 2309-2311, (1991)) disclose that the solubility of p-linked arylenes can be increased by the presence of either some m-linkages in the chain or long alkyl chains attached to the phenyl rings. However, excessive amounts of such linkages or chains may result in the loss of the desirable rigid-rod properties.

Rehahn, et al., Makromol. Chem. 191, 1990, p. 1991-2003) disclose that attaching methyl substituents does not increase the solubility of poly-p-phenylene. See, also, Percec et al., J. of Polymer Sci., Polym. chem Ed. vol 31, 1993, p. 877-1087. See, further, Percec et al., Comprehensive Polymer Science, 1st Supp., G. Allen Ed., Pergamon Press, Oxford, p. 299-385 (1992) for a discussion on the solubilization of polyphenylenes.

Marrocco, et al. (U.S. Pat. No. 5,227,457) disclose that increasing the solubility of rigid rod polymers by attaching either groups with molecular weights greater than 300, or between 15 and 300. However, this patent does not teach that the perfluoroalkyl and perfluoroalkoxy are preferred as solubility-increasing substituents, and does not exemplify these substituents.

SUMMARY OF THE INVENTION

This invention concerns a polyphenylene, comprising repeat units with the formula



(I)

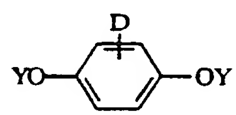
wherein

B is independently $-OC_rF_{2r+1}$ or $-C_qF_{2q+1}$, where r is 1, 2, 3 or 4 and q is 1, 2, 3 or 4;

wherein the total number of repeat units is at least about 10 and provided that (I) is at least about 50 mole percent of said repeat units.

It is most preferred if there are about 10 to 125 repeat units.

The invention also concerns a compound of the structure:



wherein

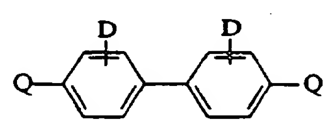
Y is independently selected from the group consisting of H and $-SO_2X$;

X is selected from the group consisting of OH, alkyl, fluoroalkyl, aryl, Br, Cl, F and I; and

each D is independently $-OC_rF_{2r+1}$ or $-C_qF_{2q+1}$, wherein r is 1, 2, 3 or 4 and q is 2, 3 or 4.

In a preferred embodiment of the structure directly above, r is 1. It is also preferred that X be selected from the group consisting of $-CH_3$, $-CF_3$, phenyl and 4-methylphenylene.

Additionally, the invention concerns a compound of the structure



wherein

Q is selected from the group consisting of OH, OSO_2X, Cl, Br and F;

X is selected from the group consisting of OH, alkyl, fluoroalkyl, aryl, Br, Cl, F and I; and

each D is independently $-OC_rF_{2r+1}$ or $-C_qF_{2q+1}$, wherein r is 1, 2, 3 or 4 and q is 2, 3 or 4.

In a preferred embodiment of the structure directly above, r is 1. It is also preferred that X be selected from the group consisting of $-CH_3$, $-CF_3$, phenyl, 4-methylphenylene and 4-fluorophenylene.

DETAILS OF THE INVENTION

Incorporation of fluorinated groups onto the backbone of poly-p-phenylenes is a useful way of not only obtaining the desirable physical properties, such as low CTE, low moisture absorption and low dielectric constant, but also improving the solubility and thereby the processibility of polyphenylenes. Applications for such materials include membranes, encapsulated, coated or shaped articles, and fibers. The fluorinated diols and their derivatives are useful as monomers for making these polyphenylenes or copolymers containing these units. One would not generally expect short-chain, fluorinated alkyl substituents to enhance polymer solubility, but surprising increases in solubility have been found with this invention. Because these perfluoroalkyl and perfluoroalkoxy chains contain at most 4 carbon atoms, the substituted poly-p-phenylenes may be made at acceptable costs; longer chains and therefore more fluorine would make the final polymers prohibitive in cost.

As taught by Rehahn, et al., Makromol. Chem. 191, 1991-2003 (1990), poly-p-phenylenes with hexyl or longer chains as substituents are completely soluble, whereas substituents of a chain length shorter than butyl are insoluble. As shown in the comparative examples, the methoxy substituted poly-p-phenylene is also insoluble in THF, DMSO, $CHCl_3$ and DMAc.

The polyphenylene of the present invention may contain 1,3-phenylene linkages provided that the percentage of 1,3-phenylene linkages does not exceed about 20% of the total number of 1,4 plus 1,3 linkages.

Polyphenylene copolymers may also be made, provided that the resulting polymer contains at least 50 mole % of repeat unit I. For example, polyphenylene

copolymers may be made containing repeat unit I together with repeat units consisting of 1,4-phenylene, 2-methyl-1,4-phenylene, 2-(4-fluorobenzoyl)-1,4-phenylene, 2,5-bis-trifluoromethyl-1,4-phenylene, 2-alkylcarboxyl-1,4-phenylene, wherein the alkyl group contains from 1 to 20 carbon atoms, 2,6-naphthylenyl, and -PhCOPh-.

In general, preferred co-monomers for the poly-p-phenylenes can be any para oriented dihalo (preferably chloride), or dihydroxy aromatic monomer. One class of these is with single or C-C connected benzene rings. Examples of these are 4,4'-dihydroxy (or dichloro) biphenyl, p-dichlorobenzene, hydroquinone, 4,4'-dihydroxy (or dichloro) p-terphenyl or p-quaterphenyl. Such materials could also be substituted on one or more aromatic rings, for example, phenylhydroquinone and substituted phenyl hydroquinone. Fused aromatic systems are also possible e.g., dihydroxy (dichloro) naphthalene (with 1,4 or 1,5 or 2,6 orientation preferred).

Comonomers can be used up to a point where the resulting copolymer is no longer soluble or otherwise processible (e.g., melt).

Similar compounds but with meta substitution could also be used in relatively small amounts without substantially detracting from the beneficial properties of the rod-like backbone. Examples of such monomers are resorcinol, m-dichlorobenzene, dichloro- or dihydroxy-m-terphenyl, 3,3'-dihydroxy (or dichloro)biphenyl. These monomers could be used up to the point where the properties of the rod-like backbone are adversely affected, e.g., lower modulus and strength, high thermal expansion coefficient.

Other potential comonomers are those with connecting groups between aromatic rings. Examples of such monomers which substantially maintain a rod-like backbone would be 4,4'-dihydroxy (or dichloro) phenyl benzamide or 4,4'-dihydroxy (or dichloro) phenyl

benzoate. Other linking groups which could be employed are -O-, C=O, SO_2, $C(CF_3)_2$, $C(CH_3)_2$, -S-. Examples of such monomers are 4,4'-dihydroxy (or dichloro) diphenyl sulfone, 4,4'-dihdroxy (or dichloro)-2,2-diphenyl hexa fluoropropane, Bisphenol A, 4,4'-dihydroxydiphenyl-ether, etc. plus other isomers and 4,4'-bis(4-hydroxy-phenoxy) diphenyl sulfone. Such groups should normally be chosen as to not seriously impact the high thermal stability of the polymer. In some cases such linking groups detract from the rod-like character of the backbone because of their non-linear nature, however, in some of these cases their isomers may not due to fact that they have highly rod-like conformations or crankshaft structures. Examples of such monomers are 3,4'-dihydroxy (or dichloro) benzophenone and 3,4'-dihydroxy (or dichloro) diphenylether. Imide or other heterocyclic (e.g., benzoxazole) linking groups can also be employed, however, these will increase the polarity of the backbone.

A wide range of copolymers is possible. In principle, any compound of one or several connected aromatic rings (connected either by direct bonding or some suitable linking group such as -O-, -S-, -SO2-, -CO-, and $=C(CF_3)_2$ is possible provided that the compounds contain the proper functionality to allow incorporation into the polymer chain. Preferably, these comonomers allow rigid, rod-like orientation to be maintained so as to maintain the desired properties. However, a small amount of flexibilizing or kinking linkages may be acceptable or even desirable for optimum polymer properties.

It is preferred that the monomers, the substituents they contain, and the linking groups be chosen and used at levels so as to not seriously detract from the thermal stability, rod-like character, or, especially for electronics applications, increase in the polarity of the system (which may increase dielectric constant and/or moisture absorption).

Copolymers of the present invention, illustrated in Examples 17-33, are soluble in contrast to the copolymers of comparative Examples C-F.

In contrast to the comparative examples, the perfluorinated alkyl- and alkoxy-substituted poly-p-phenylenes exemplified herein are soluble as shown in Examples 15 through 34.

Synthesis of Monomers

The fluorinated hydroquinones of the present invention may be prepared from the corresponding 3-(OC_rF_{2r+1})phenols or 3-(C_qF_{2q+1})phenols by an Elb reaction employing potassium persulfate as described by Feiring and Sheppard, J. Org. Chem., vol. 40, 2543 (1975). 3-(C_qF_{2q+1})phenols are known in the art and may be prepared as disclosed by Sawada et al., Jpn. Kokai Tokkyo Koho JP 020595335. 3-(OC_rF_{2r+1})phenols may be prepared by hydrolysis of the corresponding diazonium compounds generated by reaction of sodium nitrite with 1-amino-3-(OC_rF_{2r+1})benzenes. 3-Trifluoromethoxyaniline may be prepared starting from 3-aminophenol by reaction with CCl_4 and HF as described in Feiring, U.S. Pat. No. 4,157,344. More generally, 1-amino-3-(OC_rF_{2r+1})benzenes, may be prepared by reaction of 3-nitrophenols with carbonyl fluoride or a perfluoroacyl fluoride in an autoclave at 100°C, followed by reaction with SF4 as documented by Sheppard, J. Org. Chem., vol. 29, 1 (1964) and reduction of the nitro group to amino by known processes.

4,4'-dihydroxy-2,2'-bis(OC_rF_{2r+1})biphenyls may be prepared from 4,4'-diamino-2,2'-bis(OC_rF_{2r+1})biphenyl (Auman and Feiring, U.S. Pat. No. 5,175,367, 1992) by reaction with sodium nitrite followed by hydrolysis of the bis-diazonium derivative.

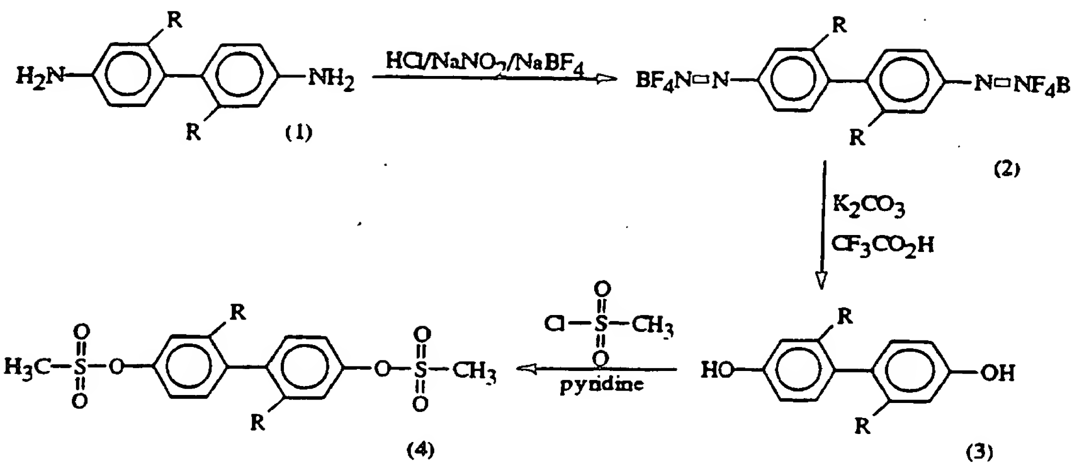
4,4'-dihydroxy-2,2'-bis(C_qF_{2q+1}) biphenyls with q > 1 may be prepared from the corresponding 4,4'-diamino-2,2'-bis(C_qF_{2q+1}) biphenyls by reaction with sodium nitrite followed by hydrolysis of the

bisdiazonium derivative. The diamino compounds may be prepared from 3-bromo- or 3-iodonitrobenzene via reaction with perfluoroalkyliodides in the presence of copper to give 3-perfluoroalkylnitrobenzenes by a method similar to that disclosed in Estes et al., U.S. Patent 5,186,985, followed by hydrazo coupling and benzidine rearrangement (U.S. Pat. 5,175,367).

Alternatively, the 4,4'-diamino-2,2'-bis(C_qF_{2q+1})biphenyl compounds may be prepared from 2,2-dibromo-4,4'-dinitrobiphenyls (Rogers et al., Macromolecules 1985, 18, 1058-1068) by reaction with perfluoroalkyliodides in the presence of copper (in a similar manner to U.S. Pat. 5,186,985) followed by catalytic hydrogenation (or other known hydrogenation method) of the nitro groups to amino groups. It is expected that the longer the perfluoroalkyl chain the lower the resulting yield of product due to steric and other effects.

Derivatives of the alcohols (phenols) may be synthesized from the alcohols (phenols) by reaction with the corresponding acid halides or anhydrides. Conditions have been described in Greene and Wuts, "Protective Groups in Organic Synthesis", 2nd edition, John Wiley & Sons, Inc., New York, 1991, pp. 168-90, or Echavarren and Stille, J. Am. Chem. Soc. 109, 1987, p. 5478.

Bisphenols as described by (3) below can be prepared according to the procedure found in Horning, et al., Can. J. of Chem. 51, p. 2347-2348 (1973). They are prepared from the diazonium salts of the corresponding benzidines according to the following scheme:



In the above structures, R is independently $-OCF_3$ or $-CF_3$.

By a repeat unit herein is meant each arylene group contained in the main polymer chain. For instance, repeat units may be 1,4-phenylene, 1,3-phenylene, 2,6-naphthylene. These repeat units may contain substitution on the aryl rings of the arylene groups. The monomers which are used to form the polymer may contribute one or more repeat units. For instance, if a biphenyl compound is used as one of the monomers, each monomer molecule contributes two repeat units to the polymer.

Synthesis of Polymers

There are various methods of synthesizing poly-p-phenylene known to those skilled in the art. Common methods include the treatment of benzene with $AlCl_3/CuCl_2$ and coupling of aryl halides via the Ullmann and Fittig reactions. See also H. Marks, et al., Ed., Encyclopedia of Polymer Science and Engineering, 2nd ed., Vol 10, John Wiley and Sons, New York, 1987, p. 673-676. In the examples below, the substituted polyphenylenes are made from substituted hydroquinones via nickel-catalyzed coupling of their bistriflates, as described in V. Percec, et al., Macromolecules 25, p. 1816-1823 (1992); Percec, U.S. Patent 5,241,044 (1993)or their bis mesylates; V. Percec et al., J. of Org. Chem., Vol. 60, p. 1066-1069

(1995). The term "triflate" refers to trifluoromethanesulfonate. Following this method, the bistriflate monomer, $Ni(Ph_3P)_2Cl_2$, zinc powder, and tetraethylammonium iodide, and optionally, triphenylphosphine, are placed in a sealed tube and dried under reduced pressure for 10 hours. THF is added via a syringe through the rubber septum, and the mixture is stirred at room temperature for 20 minutes. The color of the mixture gradually changes to a deep red brown, and is then heated at 70°C for 24 hr. After cooling to room temperature the mixture is poured into 200 mL of methanol acidified with HCl, and the precipitate collected by filtration and dissolved in 3 mL of chloroform. After another filtration to remove the zinc powder, the solution is again poured into methanol. The precipitate is again collected by filtration and dried under vacuum.

In the following examples, the following abbreviations are used:

THF = tetrahydrofuran
DMSO = dimethylsulfoxide
$CHCl_3$ = chloroform
DMAc = dimethylacetamide
$Ni(Ph_3P)_2Cl_2$ = bis(triphenylphosphine)nickel chloride
Ph_3P = triphenyl phosphine
mmol = millimole
mol = mole
eq = equivalent
OTf = triflate = trifluoromethanesulfonate
OMs = mesylate

EXAMPLE 1

Synthesis of Trifluoromethoxyhydroquinone

A round bottom flask was charged with 84.4 g (2.11 moles) NaOH in 1.05 L water. The solution was cooled in a ice/water bath and 75 g (0.42 moles) 3-trifluoromethoxyphenol was added. Under vigorous stirring 114 g (0.42 moles) potassium persulfate was

added in small portions. The ice bath was allowed to melt, the solution was stirred for 18 hours, and then was acidified by the addition of 165 mL concentrated HCl and extracted with 2 x 1 L diethyl ether. The combined ether phases were dried over magnesium sulfate and concentrated in vacuo. Distillation gave 24.94 g (0.14 mol, 33.3%) of starting material.

The aqueous solution was treated with additional 470 mL of concentrated HCl and boiled in an oil bath for 0.5 hrs. The cooled solution was extracted with 3 x 1 L of methylene chloride and the combined phases were dried over magnesium sulfate and concentrated on a rotary evaporator to a solid product. Crystallization from hexane gave 15.72 g (80.99 mmol, 19.3%) of a solid. The same compound from other preparations gave after flash-chromatography of 10.26 g (52.86 mmol) with 4:1 hexane/acetone 9.36 g (48.22 mmol) of a solid whose structure is assigned as trifluoromethoxyhydroquinone, ^{1}H-NMR (δ, DMSO-d6): 9.28 (s, 1H), 9.17 (s, 1H), 6.82 (d, 1H), 6.68-6.55 (m, 2H); ^{13}C-NMR (δ, DMSO-d6): 149.89 (s), 142.01 (s), 135.92 (s), 120.42 (q, J=255.7 Hz), 118.06 (s), 114.93 (s), 109.51 (s).

EXAMPLE 2

Synthesis of 2-Trifluoromethoxy-1,4-bis(trifluoromethylsulfonyloxy)-benzene

Trifluoromethoxyhydroquinone (2.521 g, 12.99 mmol) was dissolved in 50 mL anhydrous pyridine and cooled with an ice/salt-bath to -10°C. Then slowly 5.1 mL (2.33 eq.) trifluoromethanesulfonic anhydride (triflic anhydride) were added with a syringe. The solution turned dark red and was allowed to warm up to room temperature and stirred for 24 hours. This reaction mixture was poured on water and extracted three times with diethyl ether. The combined organic layers were washed once with water, twice with 10% aqueous HCl, twice with water and twice with saturated NaCl solution. After drying with magnesium sulfate the organic layer was evaporated on a rotary evaporator

giving 5.86 g of a yellow oil. After flash chromatography with petroleum ether a colorless liquid product was obtained. The distilled product crystallized. (Yield: 5.362 g, 90.0%). ^{19}F-NMR (δ, $CDCl_3$): -73.74 (TfO), -72.95 (TfO), -58.88 (OCF_3).

The same compound from other preparations gave ^{1}H-NMR (δ, $CDCl_3$): 7.54 (d, 1H, J=9 Hz), 7.42-7.32 (m, 2H); ^{13}C-NMR (δ, CDC13): 148.01 (s), 141.50 (s), 140.16 (s), 125.09 (s), 121.07 (s), 120.11 (q, J=262.9 Hz), 118.70 (q, J=321 Hz), 118.63 (q, J=321 Hz), 116.31 (s).

EXAMPLE 3

Synthesis of 2-Trifluoromethyl-1,4-bis(trifluoromethylsulfonyloxy)benzene

This reaction was performed in the same manner as in Example 2 from trifluoromethylhydroquinone. Yield: 67.8%. ^{19}F-NMR (δ, $CDCl_3$): -73.74 (TfO), -72.92 (TfO), -61.84 (CF3); ^{1}H-NMR (δ, CDC13): 7.70-7.58 (m, 3H); ^{13}C-NMR (δ, $CDCl_3$): 147.59 (s), 145.22 (s), 127.02 (s), 125.56 (q, J=34.2 Hz), 124.70 (s), 121.77 (q, J=4.7 Hz), 120.94 (q, J=274 Hz), 118.73 (q, J=321 Hz), 118.46 (q, J=320 Hz); mp: 15.8°C. The same compound from other preparations gave 90% yield.

EXAMPLE 4

Synthesis of 2,2'-Bis(trifluoromethoxy)-4,4'-dihydroxybiphenyl

2,2'-Bis(trifluoromethoxy)-4,4'-dihydroxybiphenyl(3.705 g, 10.518 mmol) was dissolved in a solution of 22 mL HCl and 100 mL water and cooled with an ice bath to 5°C. A solution of 1.45 g (21.0 mmol) sodium nitrite in 10 mL water was added so that the temperature remained between 0 and 5°C. This solution was added to a cool solution of 20 mL phosphoric acid and 1.8 L water. After stirring for 5 minutes the orange mixture was heated to the boiling point. Evolution of a gas was observable. After boiling for 10 minutes the mixture was cooled and extracted with diethyl ether. The organic phase was extracted with 2N NaOH soution, the aqueous phase was acidified with

concentrated HCl and extracted with diethyl ether. The solvent was evaporated. After drying under high vacuum, an orange product was isolated. This product was combined with the product of a second reaction, which was performed in the same manner from 7.99 g (22.68 mmol) starting material. These combined raw materials were purified by a sublimation at 140°C/0.02 mm. It resulted in 7.708 g (65.5% yield) of a slightly yellowish material. ^{19}F-NMR (δ, DMSO-d6): -55.72 (OCF_3); ^{1}H-NMR(δ,DMSO-d6)10.15 (s, 2H), 7.18 (d, 2H, J=8.4 Hz), 6.86 (dxd, 2H, J=8.4 Hz, J=2.4 Hz), 6.83 (d, 2H, J=2.4 Hz); ^{13}C-NMR (δ, DMSO-d6): 158.23 (s), 148.50 (s), 132.69 (s), 119.99 (q, J=256.50 Hz), 119.81 (s), 114,29 (s), 107.10 (s); mp: 145°C.

EXAMPLE 5

Synthesis of 2,2'-Bis(trifluoro-methoxy)-4,4'-dihydroxybiphenyl (3a)

Concentrated hydrochloric acid (70 mL) was added to a stirred suspension of the 2,2'-bis(trifluoro-methoxy) benzidine (70 mmole, 24.7 g) in water (140 mL) and the mixture thus obtained was cooled to 0°C and treated with a solution of sodium nitrite (10.6 g) in water (20 mL). After 20 min. at 0°C a solution of sodium tetrafluoroborate (22 g) in water (70 mL) was added, and after 30 min. the product (diazonium tetrafluoroborate) was collected by filtration, washed with a small amount of ice-water and then with 100 mL of ether. The product was dried in vacuum 12 h.

Potassium carbonate (3.8 g) was added at 0°C to trifluoroacetic acid (120 mL), and then the diazonium tetrafluoroborate (13 g) was added. The resultant was stirred at reflux temperature for 28 h. The solution was added to water (300 mL), and the solid wad collected by filtration and recystallized from ethanol. The slight yellow crystal thus obtained (9.0 g, 73%) ^{1}H NMR: δ 7.02-7.06 (m, 4H), 7.28 (d, J=9 Hz, 2H).

EXAMPLE 6

Synthesis of 2,2'-Bis(trifluoromethoxy)-
4,4'-bis(trifluoromethylsulfonyloxy)biphenyl

4,4'-Dihydroxy-2,2'-bis(trifluoromethoxy)biphenyl (7.70 g, 21.7 mmol) was dissolved in 80 mL anhydrous pyridine and cooled to -10°C with an ice/salt bath. 9.1 mL (2.5 eq.) triflic anhydride were added dropwise with a syringe. The solution turned dark-red and precipitation was observed. This precipitate disappeared as the temperature rose to room temperature. The solution was stirred for 16 hours and worked up as described in Example 2. After the chromatography the product was sublimed at 118°C/0.01 mm, and 12.1 g (90.2%) of a white material was obtained. ^{19}F-NMR (δ, $CDCl_3$): -73.06 (OTf), -58.29 (OCF_3); ^{1}H-NMR (δ, $CDCl_3$): 7.47 (d, 2H, J=8.6 Hz), 7.37 (dxd,2H, J=8.5 Hz, J=2.4 Hz), 7.35 (d, 2H, J=2.4 Hz); ^{13}C-NMR (δ, $CDCl_3$): 149.61 (s), 147.60 (s), 133.00 (s), 128.59 (s), 120.13 (q, J=267), 119.91 (s), 118.77 (q, J=321 Hz), 114.38 (s); mp: 73.2°C.

EXAMPLE 7

Synthesis of 2,2'-Bis(trifluoro-
methyl)-4,4'-dihydroxybiphenyl

This compound was prepared from 2,2'-bis(trifluoromethyl)benzidine using the method in Example 5. The slight yellow oil was obtained (15 g, 74%). ^{1}H NMR: δ 7.00 (d, J=8 Hz, 2H) 7.10-7.27 (m, 4H).

EXAMPLE 8

Synthesis of 2,2'-Bis(trifluoromethyl)-
4,4'-bis(trifluoromethylsulfonyloxy)biphenyl

4,4'-Dihydroxy-2,2'-bis(trifluoromethyl)biphenyl (4.20 g, 13.04 mmol) was dissolved in 50 mL anhydrous pyridine and cooled to -10°C. Slowly 6 mL (2.7 eq.) triflic anhydride was added and the solution was stirred overnight and allowed to warm up to room temperature. The reaction was worked up as described in Example 2. After chromatography a yield of 5.362 g

(70.1%) was obtained. ^{19}F-NMR (δ, $CDCl_3$): -73.07 (OTf), -59.19 (CF_3); ^1H-NMR (δ, $CDCl_3$): 7.69 (d, 2H, J=2.5 Hz), 7.55 (dxd, 2H, J=8.6 Hz, J=2.5 Hz), 7.45 (d, 2H, J=8.6 Hz); ^{13}C-NMR (δ, $CDCl_3$): 149.27 (s), 135.82 (s), 133.77 (s), 131.46 (q, J=32.4 Hz), 124.17 (s), 122.46 (q, J=275 Hz), 119.93 (s), 118.82 (q, J=321 Hz); mp: 48.4°C.

EXAMPLE 9

Synthesis of 2,2'-Bis(trifluoromethoxy)-4,4'-Bis(methylsulfonyloxy)biphenyl

The aryl mesylates were prepared by the reaction of methanesulfonyl chloride with the bisphenol in pyridine.

A 100 mL flask was charged with bisphenol of Example 5 (7.1 g, 20 mmole) and 50 mL of pyridine and 0.1 g of dimethylamino pyridine. Methanesulfonyl chloride (6.9 g, 60 mmole) was dropped to the solution at 0°C under nitrogen. The mixture was stirred at 0°C for 1 h and at 23°C for 12 h. The crude product was collected by adding water and filtration. After recrystallization from ether and hexane (1:1). The colorless crystals were obtained (6.5 g, 64%). ^1H NMR: δ 3.24 (s, 6H), 7.33-7.39 (m, 6H).

EXAMPLE 10

Synthesis of 2,2'-Bis(trifluoromethyl)-4,4'-Bis(methylsulfonyloxy)biphenyl

This compound was prepared by the same method as for Example 9. Slight yellow crystals were obtained (16.1 g, 72%). ^1H NMR: δ 3.26 (s, 6H), 7.36 (d, J=8, 2H), 7.51 (d, J=8, 2H), 7.67 (d, J=2, 2H).

EXAMPLE 11

Polymerization of 2-Trifluoromethoxy-1,4'-bis(trifluoromethylsulfonyloxy)benzene

A 50 mL round bottom flask with reflux condenser was filled under nitrogen with 0.216 g (0.33 mmol) $Ni(Ph_3P)_2Cl_2$, 1.678 g (25.67 mmol) zinc dust and 0.790 g (3.07 mmol) tetraethylammonium iodide. The flask was evacuated three times and purged with

nitrogen. Then 1 mL THF (freshly distilled over Na) was added and the mixture was stirred for 5 minutes. A color change to dark red was observed. Then 1.17 g (2.55 mmol) 2-trifluoromethoxy-1,4-bis(trifluoromethylsulfonyloxy)benzene was added with a syringe. The temperature was raised to 70°C. After 1 hour the oil bath was removed and the suspension was allowed to cool. The reaction mixture was poured into 100 mL methanol acidified with concentrated HCl. The precipitate was filtered off and dried. The solid was dissolved in 10 mL chloroform and filtered. The chloroform solution was poured into methanol acidified with concentrated HCl. After filtration and drying 0.183 g (44.8%) of a white polymer was obtained. GPC (THF, PS Standard): Mn=7560, Mw=16700; ^{1}H-NMR (δ, $CDCl_3$):7.8-7.4 (m, broad); ^{19}F-NMR (δ, $CDCl_3$): -57.91 (m), -57.57 (m); IR (KBr): 2952 (w), 2922 (m), 2851 (m), 1617 (w), 1478 (m), 1390 (w), 1266 (s), 1167 (s), 818 (m). The same compound from other preparations gave a weak UV absorption in THF: UV(THF, 1 cm): λ max = 307 nm; ε = 85.

EXAMPLE 12

Polymerization of 2,2'-Bis(trifluoromethoxy)-4,4'-bis(trifluoromethylsulfonyloxy)biphenyl

This reaction was carried out as in Example 11 except that the monomer was dissolved in 4 mL THF and the polymer was redissolved in THF and not in chloroform, after precipitation and drying. Starting materials were 4 mL THF, 0.982 g (1.50 mmol) $Ni(Ph_3P)_2Cl_2$, 7.49 g (0.115 mol) zinc dust, 3.58 g (13.9 mmol) tetraethylammonium iodide and 6.92 g (11.19 mmol) 2,2'-bis(trifluoromethoxy)-4,4'-bis(trifluoromethylsulfonyloxy)biphenyl in 4 mL THF. Yield: 0.328 g. GPC (THF, PS Standard): Mn=54500, Mw=99400; ^{1}H-NMR (δ, THF-d8): 8.0-7.4 (m, broad); ^{19}F-NMR (δ, THF-d8): -56.49 (m); IR (KBr): 1614 (w), 1478 (m), 1391 (w), 1271 (s), 1264 (sh), 1250 (s), 1216 (s), 1167 (s), 820 (m); UV (THF, 1 cm): λ max=302 nm; ε = 76.

EXAMPLE 13

Polymerization of 2-Trifluoromethyl-1,4-bis(trifluoromethylsulfonyloxy)benzene

This reaction was carried out as in Example 11 except the polymer was redissolved in THF and not in chloroform after precipitation and drying. Starting materials were 7 mL THF, 0.998 g (1.53 mmol) $Ni(Ph_3P)_2Cl_2$, 7.76 g (0.119 mol) zinc dust, 3.65 g (14.2 mmol) tetraethylammonium iodide and 8.77 g (19.8 mmol) 2-trifluoromethyl-1,4-bis(trifluoromethylsulfonyloxy)benzene. Yield: 0.518 g. GPC (THF, PS Standard): Mn=12400, Mw= 17300; ^1H-NMR (δ, THF-d8): 8.4-7.5 (m, broad); ^{19}F-NMR (δ, THF-d8): -57.52 (m, CF3), -56.24 (m, CF3), very weak: -73.93 (OTf), -73.88 (OTf); IR (KBr): 1617 (w), 1480 (m), 1430 (w), 1428 (w), 1411 (w), 1394 (sh), 1325 (s), 1292 (m), 1252 (m), 1175 (s), 1136 (s), 1087 (w), 1069 (w), 1060 (w), 1047 (w), 1026 (w), 1005 (w), 900 (w), 833 (w), 653 (w); UV (THF, 1 cm): λ max=271 nm; ε = 74.

EXAMPLE 14

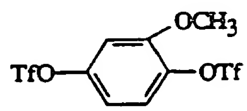
Polymerization of 2,2'-Bis(trifluoromethyl)-4,4'-bis(trifluoromethylsulfonyloxy)biphenyl

This reaction was carried out as in Example 11, except the monomer was dissolved in 4 mL THF and the polymer was redissolved in THF and not in chloroform after precipitiation and drying. Starting materials were 2 mL THF 0.677 g (1.035 mmol) $Ni(Ph_3P)_2Cl_2$, 5.031 g (76.95 mmol) zinc dust, 2.395 g (9.313 mmol) tetraethylammonium iodide and 4.529 g (7.725 mmol) 2,2'-bis(trifluoromethyl)-4,4'-bis(trifluoromethylsulfonyloxy)biphenyl in 4 mL THF. Yield: 0.814 g. GPC (THF, PS Standard): Mn=9450, Mw=18800; ^1H-NMR (δ, THF-d8): 8.27 (s (b), 1H), 8.14 (d, 1H, J=7.3), 7.60 (d, 1H, J=7.2); ^{19}F-NMR (δ, THF-d8): -57.50 (CF3), very weak: -73.11 (OTf); IR (KBr): 1480 (m), 1422 (w), 1408 (w), 1388 (m), 1313 (s), 1285 (sh), 1249 (m), 1174 (s), 1134 (s), 1084 (m), 1059 (w), 1047 (w), 1002 (w), 916

(w), 900 (w), 834 (w), 681 (w), 556 (w); UV (THF, 1 cm): λ max=273 mn; ε = 90.

COMPARATIVE EXAMPLE A

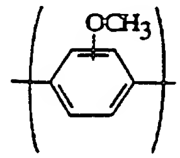
Synthesis of 2-Methoxy-1,4-bis(trifluoromethylsulfonyloxy)-benzene



Methoxyhydroquinone (5.800 g, 46.72 mmol) was dissolved in 180 mL anhydrous pyridine and cooled with an ice/salt-bath to -10°C. Then slowly 19.0 mL (2.4 eq) trifluoromethanesulfonic anhydride (triflic anhydride) were added with a syringe. The solution turned dark red and was allowed to warm up to room temperature and stirred for 24 hours. This reaction mixture was poured on water and extracted three times with diethyl ether. The organic combined organic layer was washed once with water, twice with 10% aqueous hydrochloric acid, twice with water and twice with saurated sodium chloride solution. After drying with magnesium sulfate the organic layer was evaporated on a rotary evaporator giving an orange solid. Sublimation at 74°C/0.05 mm gave 14.54 g (80.1%) of a white solid. MP 69°C. ^{19}F-NMR (δ, DMSO): -73.25, -72.23; ^{1}H-NMR (δ, DMSO): 7.70 (d, 1H, J=9.1 Hz), 7.62 (d, 1H, J=2.9 Hz), 7.23 (dxd, 1H, J=2.9 Hz, J=9.1 Hz), 3.97 (s, 3H); ^{13}C-NMR (δ, DMSO): 152.18 (s), 148.82 (s), 137.46 (s), 124.15 (s), 118.26 (q, J=321 Hz), 118.22 (q, J=320 Hz), 113.92 (s), 108.64 (s), 57.50 (s).

COMPARATIVE EXAMPLE B

Polymerization of 2-Methoxy-1,4-bis(trifluoromethylsulfonyloxy)benzene



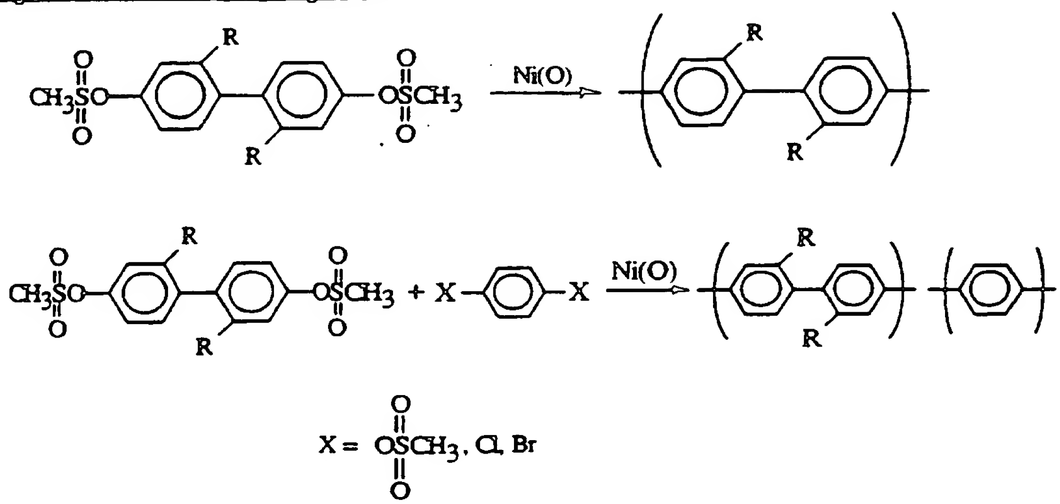
A 50 mL round bottom flask with reflux condenser was filled under nitrogen with 0.430 g (0.657 mmol) $Ni(Ph_3P)_2Cl_2$, 3.141 g (48.04 mmol) zinc dust and 1.479 g (5.75 mmol) tetraethylammonium iodide. The flask evacuated three times and purged with nitrogen. Then 2 mL THF (freshly distilled over sodium) was added and the mixture was stirred for 5 minutes. A color change to dark red was observed. Then 1.846 g (4.75 mmol) 2-methoxy-1,4-bis(trifluoromethylsulfonyloxy)benzene dissolved in 3 mL THF (freshly distilled over sodium) was added with a syringe. The temperature was raised to 70°C. After 1 hour the oil bath was removed and the suspension was allowed to cool. The reaction mixture was poured into 100 mL methanol acidified with concentrated HCl. The polymer was washed with a solution of 10% HCl in methanol to get rid of the zinc. Yield was 44.8%. IR (KBr): 3436 (s), 2996 (w), 2952 (w), 2953 (w), 2910 (w), 2831 (w), 1604 (s), 1569 (m), 1480 (s), 1463 (s), 1419 (m), 1388 (s), 1306 (m), 1288 (w), 1260 (m), 1238 (s), 1216 (s), 1179 (m), 1139 (m), 1039 (m), 1027 (m), 1003 (m), 944 (w), 892 (w), 854 (w), 813 (m), 752 (w), 724 (w), 703 (w). The same compound from other preparations gave a TGA onset 442°C, 10% weight loss 456°C. This compound was insoluble in THF, chloroform, DMSO and DMAc.

EXAMPLES 15 THROUGH 33

Procedure of Polymerization

The same polymerization method was used for Examples 15 through 33 and comparative Examples B through F. A typical polymerization example is provided below, and can be shown as the following scheme:

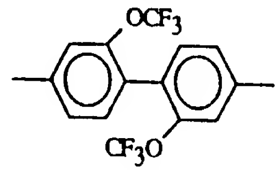
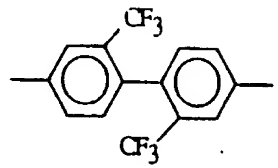
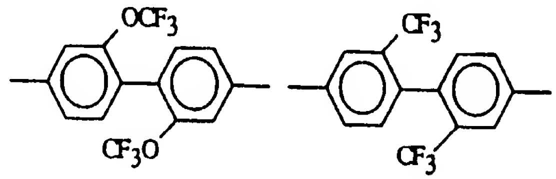
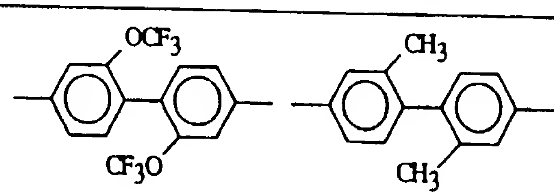
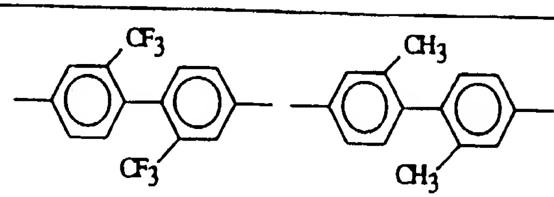
Synthesis of Polymers

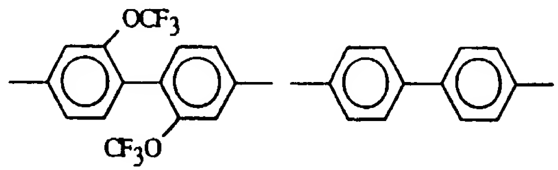
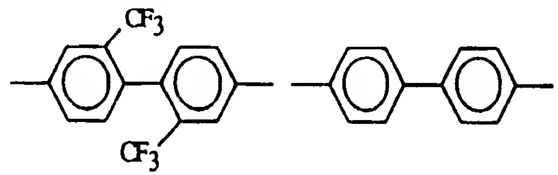
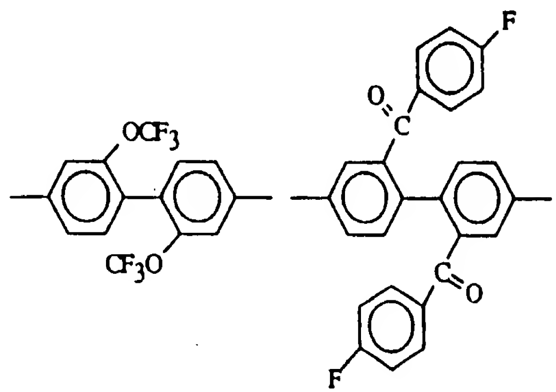


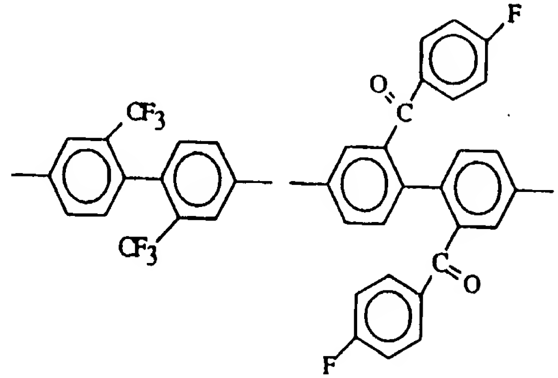
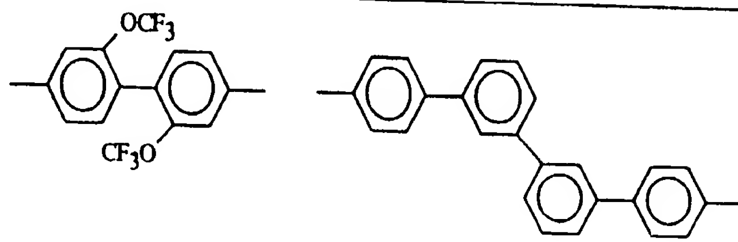
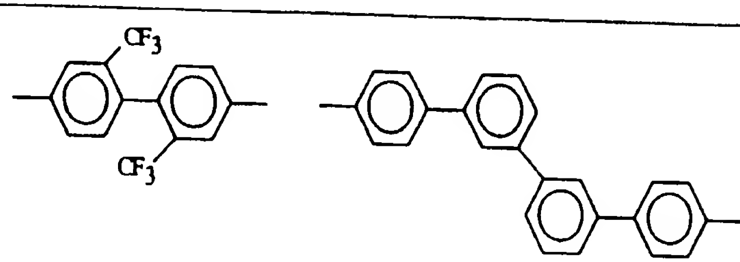
The monomer 2,2-bis(trifluoromethyl)-4,4'-di(methanesulfonyloxy)biphenyl (0.837 g, 1.75 mmol), $Ni(Ph_3P)_2Cl_2$ (0.115 g, 0.175 mmole) Zn powder (0.801 g, 12.25 mmol), Et_4NI (0.675 g, 2.63 mmole) and Ph_3P (0.275 g, 1.05 mmol) were placed in a 125 mL Schlenk tube with a magnetic stirring bar. After sealing the tube with a rubber septum, the contents were dried at 22°C under reduced pressure for 10 h. The evacuation and filling with Ar was repeated four times. 2.0 mL of freshly distilled THF was added via a syringe through the rubber septum. The mixture was stirred at room temperature for 20 min. and during this time the color of the mixture gradually changed deep red brown. The reaction mixture was heated at 70°C oil bath for 24 h. After cooling to room temperature the mixture was poured into 200 mL of methanol acidified with HCl. The precipitate was collected by filtration and dissolved in 3 mL of $CHCl_3$. The solution was filtered to remove Zn powder and poured into methanol. The precipitate was collected by filtration and vacuum dried. The yield was 0.42 g (83%). Mn (GPC) = 4690, Mw/Mn = 2.4.

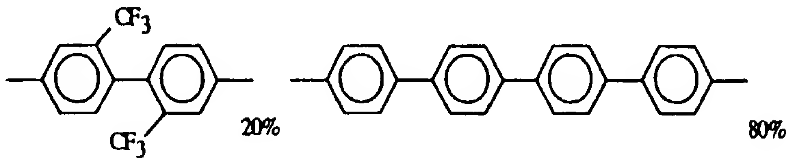
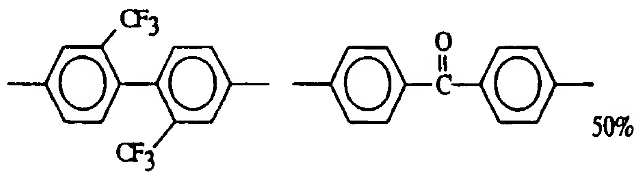
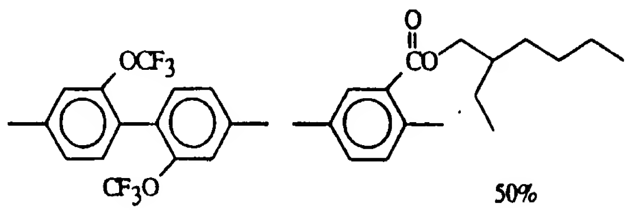
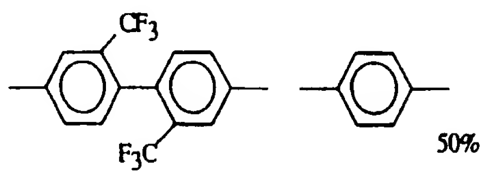
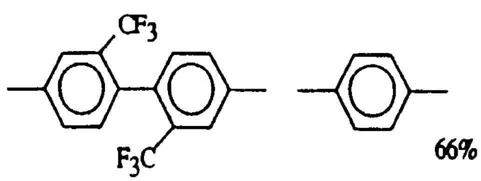
Table 1 illustrates the solubility of the homopolymers and copolymers of the present invention. Numerical data for Mn and Mw/Mn indicates polymers sufficiently soluble in THF for determination by GPC.

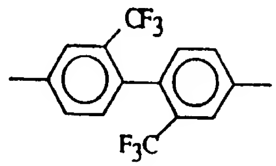
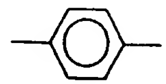
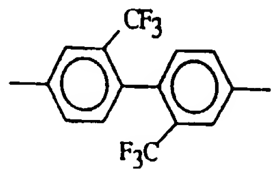
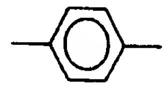
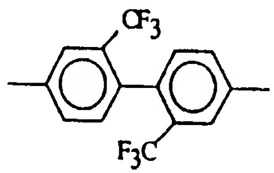
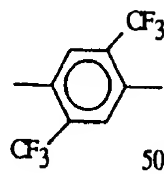
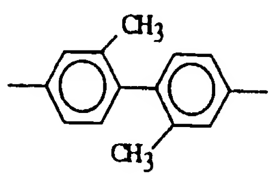
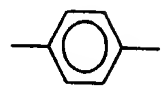
TABLE 1

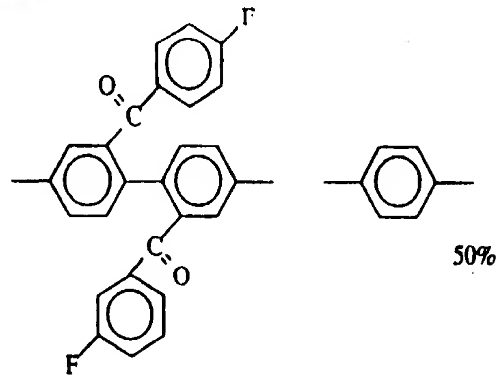
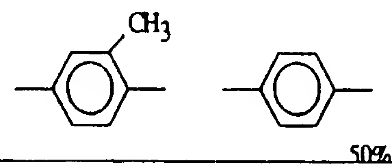
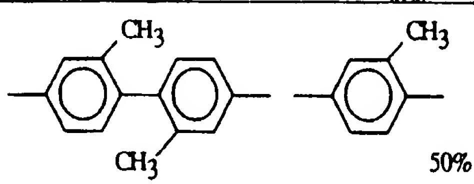
Example No.	Monomeric Units	Yield (%)	Mn	Mw/Mn	Tg (°C)	dec. temp (°C)[a]
15		86	All soluble in DMF, insoluble in THF			420
16		81	8370	4.0		455
17	 50%	87	20600	2.9		430
18	 50%	90	Soluble in DMF			380
19	 50%	78	9430	2.8		380

20	 50%	100	Not all soluble in DMF		124	405
21	 50%	88	6270	2.5	173	400
22	 50%	83	16630	2.9	162	375

23	 50%	92	10680	3.0		355
24	 50%	98	Soluble in DMF			383
25	 50%	85	14670	2.6	152	382

26		96	Not All Soluble DMF		
27		90	5440	2.2	300
28		85	8040	3.1	
29		75	7180	2.8	412
30		84	5950	2.5	395

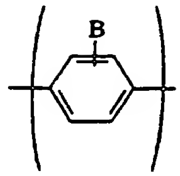
31		 50%	69	6240	2.7		390
32		 50%	81	7340	2.4		410
33		 50%	64	4410	2.0	146	342
Comp. Ex. C		 50%	89	Insoluble			

Comp. Ex. D		92	Insoluble
Comp. Ex. E		82	Insoluble
Comp. Ex. F		87	Insoluble

[a]Temperature at 10% weight loss recorded by Tg at a heating rate of 20°C/min. in N_2. (Perkin Elmer DSC 7)

What is claimed is:

1. A polyphenylene comprising repeat units with the formula



(I)

wherein

each B is independently $-OC_rF_{2r+1}$ or $-C_qF_{2q+1}$, where r is 1, 2, 3 or 4 and q is 1, 2, 3, or 4

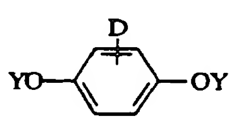
wherein the total number of repeat units is at least about 10, and provided that (I) is at least about 50 mole percent of said repeat units.

2. The polyphenylene as recited in Claim 1 wherein the total number of repeat units is about 10 to about 125.

3. The polyphenylene as recited in Claim 1 wherein r is 1 and q is 1.

4. The polyphenylene of Claim 1 wherein such polyphenylene contains 1,3-phenylene linkages, provided that the percentage of 1,3-phenylene linkages does not exceed about 20% of the total number of 1,4 plus 1,3 linkages.

5. A compound of the structure



wherein

Y is selected from the group consisting of H and $-SO_2X$;

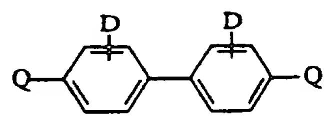
X is selected from the group consisting of H, alkyl, fluoroalkyl, aryl, Br, Cl, F and I;

and each D is independently $-OC_rF_{2r+1}$ or $-C_qF_{2q+1}$, where r is 1, 2, 3 or 4 and q is 2, 3 or 4.

6. The compound as recited in claim 5 wherein r is 1.

7. The compound as recited in claim 5 wherein X is selected from the group consisting of $-CH_3$, $-CF_3$, phenyl or 4-methylphenylene.

8. A compound of the structure



wherein

Q is selected from the group consisting of OH, OSO_2X, Cl, Br and F;

X is selected from the group consisting of H, alkyl, fluoroalkyl, aryl, Br, Cl, F and I; and

each D is independently $-OC_rF_{2r+1}$ or $-C_qF_{2q+1}$, where r is 1, 2, 3 or 4 and q is 2, 3 or 4.

9. The compound as recited in claim 8 wherein r is 1.

10. The compound as recited in claim 8 wherein X is selected from the group consisting of $-CH_3$, $-CF_3$, phenyl or 4-methylphenylene.

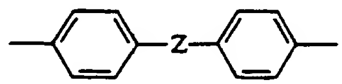
11. A copolymer comprising repeat unit (I) of claim 1 and one or more other repeat units, provided that the repeat unit (I) comprises at least 50 percent of the total repeat units.

12. The copolymer as recited in claim 10 wherein the other repeat units are para oriented aromatic groups.

13. The copolymer as recited in Claim 11 wherein such copolymer contains 1,3-phenylene linkages, provided that the percentage of 1,3-phenylene linkages does not exceed about 20% of the total number of 1,4 plus 1,3 linkages.

14. The copolymer as recited in Claim 12 wherein the other repeat units are selected from the group

consisting of 1,4-phenylene, 2-methyl-1,4-phenylene, 2-(4-fluorobenzoyl)-1,4-phenylene, 2,5-bis-trifluoromethyl-1,4-phenylene, 2-alkylcarboxyl-1,4-phenylene, wherein the alkyl group contains from 1 to 20 carbon atoms, 2,6-naphthylenyl, or



wherein Z is -C(=O)NH-, C=O, -C(=O)O, O, S, SO_2, 3,4'-diphenylene, 3,3'-diphenylene, $C(CH_3)_2$, $C(CF_3)_2$, 1,4'phenylene, 4,4'-diphenylene, or nothing.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 96/02550

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G61/10 C07C43/23 C07C39/24 C07C43/225

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,40 00 048 (BAYER AG) 4 July 1991 see claims 1,2 see page 7, line 22 - line 26 ---	1-3,11, 12,14
X	EP,A,0 348 717 (BAYER AG) 3 January 1990 see claims 1,2 see page 12, line 17 see page 12, line 25 ---	1-3,11, 12,14
A	WO,A,89 07617 (MAXDEM INC.) 24 August 1989 see claims 1,17,21,22 see page 56, line 31 ---	1-14

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
9 July 1996	29.07.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	O'Sullivan, T

INTERNATIONAL SEARCH REPORT

Inv ional Application No
PCT/US 96/02550

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ADVANCED MATERIALS , vol. 6, no. 3, March 1994, WEINHEIM ,DE, pages 190-198, XP002007916 see page 193, column 1, paragraph 2 ---	1,4,13
X	TETRAHEDRON , vol. 48, no. 39, 1992, G.B., pages 8353-8368, XP002007917 UNO H. ET AL: "Perfluoroalkyl migration in the rearrangement of 4-perfluoroalkyl-4-quinols" * Formula 4c * see page 8354 ---	5-7
A	US,A,4 433 132 (RODGERS H.G. ET AL) 21 February 1984 see column 2, line 25 - line 35 -----	8-10

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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 96/02550

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE-A-4000048	04-07-91	NONE		
EP-A-0348717	03-01-90	DE-A-	3821567	28-12-89
		JP-A-	2045521	15-02-90
		US-A-	5102971	07-04-92
WO-A-8907617	24-08-89	EP-A-	0401296	12-12-90
		JP-T-	3502815	27-06-91
		US-A-	5227457	13-07-93
US-A-4433132	21-02-84	US-A-	4628125	09-12-86

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08G 61/10, C07C 43/23, 39/24, 43/225 | A1

(11) International Publication Number: WO 96/28491

(43) International Publication Date: 19 September 1996 (19.09.96)

(21) International Application Number: PCT/US96/02550

(22) International Filing Date: 7 March 1996 (07.03.96)

(30) Priority Data:
08/402,278 10 March 1995 (10.03.95) US

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(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
With amended claims.

Date of publication of the amended claims: 31 October 1996 (31.10.96)

(54) Title: SOLUBLE FLUORINATED POLY-P-PHENYLENES

(57) Abstract

Disclosed are poly-p-phenylenes which have perfluoroalkoxy and perfluoroalkyl substituents, their copolymers and the precursors to these polymers. Polymers produced herein are useful as membranes, coatings, fibers and articles.

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AMENDED CLAIMS

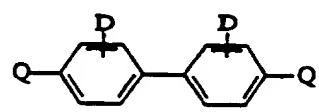
[received by the International Bureau on 11 September 1996 (11.09.96); original claim 5 amended; remaining claims unchanged (1 page)]

and each D is independently $-OC_rF_{2r+1}$ or $-C_qF_{2q+1}$, where r is 1, 2, 3 or 4 and q is 1, 2, 3 or 4; provided that when Y is H, D is $-OC_rF_{2r+1}$.

6. The compound as recited in claim 5 wherein r is 1.

7. The compound as recited in claim 5 wherein X is selected from the group consisting of $-CH_3$, $-CF_3$, phenyl or 4-methylphenylene.

8. A compound of the structure



wherein

Q is selected from the group consisting of OH, OSO_2X, Cl, Br and F;

X is selected from the group consisting of H, alkyl, fluoroalkyl, aryl, Br, Cl, F and I; and

each D is independently $-OC_rF_{2r+1}$ or $-C_qF_{2q+1}$, where r is 1, 2, 3 or 4 and q is 2, 3 or 4.

9. The compound as recited in claim 8 wherein r is 1.

10. The compound as recited in claim 8 wherein X is selected from the group consisting of $-CH_3$, $-CF_3$, phenyl or 4-methylphenylene.

11. A copolymer comprising repeat unit (I) of claim 1 and one or more other repeat units, provided that the repeat unit (I) comprises at least 50 percent of the total repeat units.

12. The copolymer as recited in claim 10 wherein the other repeat units are para oriented aromatic groups.

13. The copolymer as recited in Claim 11 wherein such copolymer contains 1,3-phenylene linkages, provided that the percentage of 1,3-phenylene linkages does not exceed about 20% of the total number of 1,4 plus 1,3 linkages.

14. The copolymer as recited in Claim 12 wherein the other repeat units are selected from the group